09/076,566

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



ATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C	A2	(11) International Publication Number: WO 99/58462 (43) International Publication Date: 18 November 1999 (18.11.99)
(21) International Application Number: PCT/US (22) International Filing Date: 11 May 1999 ((30) Priority Data:	1 1	BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD,

(71) Applicant: PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US).

12 May 1998 (12.05.98)

- (72) Inventors: KRUMWIEDE, John, F.; 315 Blue Run Road, Cheswick, PA 15024 (US). SHELESTAK, Larry, J.; 1046 Ford Street, P.O. Box 233, Bairdford, PA 15006 (US).
- (74) Agents: STACHEL, Kenneth, J.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.
- ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

Without international search report and to be republished upon receipt of that report.

(54) Title: BLUE PRIVACY GLASS

(57) Abstract

The present invention provides a blue colored, infrared and ultraviolet absorbing glass composition having a luminous transmittance of up to 60 percent. The glass uses a standard soda-lime-silica glass base composition and additionally iron and cobalt, and optionally selenium and/or titanium, as infrared and ultraviolet radiation absorbing materials and colorants. The glass of the present invention has a color characterized by a dominant wavelength in the range of 480 to 489 nanometers and an excitation purity of at least 8 percent at a thickness of 0.160 inches (4.06 millimeters). In one embodiment of the invention, the glass composition of a blue colored, infrared and ultraviolet radiation absorbing soda-lime-silica glass article includes a solar radiation absorbing and colorant portion consisting essentially of 0.9 to 2.0 percent by weight total iron, 0.15 to 0.65 percent by weight FeO, 90 to 250 PPM CoO, and optionally up to 12 PPM Se and up to 0.9 wt.% TiO2, and preferably 1 to 1.4 percent by weight total iron, 0.20 to 0.5 percent by weight FeO, 100 to 150 PPM CoO, up to 8 PPM Se, and up to 0.5 wt.% TiO₂.

ISDOCID: <WO_

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES Spain	LS Lesotho	SI Slovenia
AM ·	Armenia	FI Finland	LT Lithuania	SK Slovakia
AT	Austria	FR France	LU Luxembourg	SN Senegal
AU	Australia	GA Gabon	LV Latvia	SZ Swaziland
AZ	Azerbaijan	GB United Kingdom	MC Monaco	TD Chad
BA	Bosnia and Herzegovina	GE Georgia	MD Republic of Moldova	TG Togo
BB	Barbados	GH Ghana	MG Madagascar	TJ Tajikistan
BE	Belgium	GN Guinea	MK The former Yugoslav	TM Turkmenistan
BF	Burkina Faso	GR Greece	Republic of Macedonia	TR Turkey
BG .	Bulgaria	HU Hungary	ML Mali	TT Trinidad and Tobago
BJ	Benin	IE Ireland	MN Mongolia	UA Ukraine
BR	Brazil	IL Israel	MR Mauritania	UG Uganda
BY	Belarus	IS Iceland	MW Malawi	US United States of America
CA	Canada	IT Italy	MX Mexico	UZ Uzbekistan
CF	Central African Republic	JP Japan	NE Niger	VN Viet Nam
CG	Congo	KE Kenya	NL Netherlands	YU Yugoslavia
СН	Switzerland	KG Kyrgyzstan	NO Norway	ZW Zimbabwe
CI	Côte d'Ivoire	KP Democratic People's	NZ New Zealand	
CM	Cameroon	Republic of Korea	PL Poland	
CN	China	KR Republic of Korea	PT Portugal	
CU	Cuba	KZ Kazakstan	RO Romania	
CZ	Czech Republic	LC Saint Lucia	RU. Russian Federation	
DE	Germany	LI Liechtenstein	SD Sudan	
DK	Denmark	LK Sri Lanka	SE Sweden	
EE	Estonia	LR Liberia	SG Singapore	
	Lations		나는 이 중 전 시계를 받는다.	

WO 99/58462 PCT/US99/10295

BLUE PRIVACY GLASS

BACKGROUND OF THE INVENTION

1. Field of the Invention

5

This invention relates to a blue colored soda-lime-silica glass having a low luminous transmittance that makes it desirable for use as a privacy glazing in vehicles, such as the side and rear windows in vans or sun roofs for automotive vehicles. As used herein, the term "blue colored" is meant to include glasses that have a dominant wavelength of 480 to 489 nanometers (nm) and may also be characterized as blue-green or blue-gray in color. In addition, the glass should exhibit lower infrared and ultraviolet radiation transmittance when compared to typical blue glasses used in automotive applications and be compatible with float glass manufacturing methods.

2. <u>Technical Considerations and Prior Art</u>

Various dark tinted, infrared and ultraviolet radiation absorbing glass compositions are known in the art. The primary colorant in typical dark tinted automotive privacy glasses is iron, which is usually present in both the Fe₂O₃ and FeO forms. Some glasses use cobalt, selenium and, optionally, nickel in combination with iron to achieve a desired color and infrared and ultraviolet radiation, for example, as disclosed in U.S. Patent Nos. 4,873,206 to Jones; 5,278,108 to Cheng, et al.; 5,308,805 to Baker, et al.; 5,393,593 to Gulotta, et al.; 5,545,596 and 5,582,455 to Casariego, et al.; and European Patent Application No. 0 705 800. Others also include chromium with this combination of colorants as disclosed in U.S. Patent Nos. 4,104,076 to Pons; 4,339,541 to Dela Ruye; 5,023,210 to Krumwiede, et al.; and 5,352,640 to Combes, et al.; European Patent Application No. 0 536 049; French Patent No. 2,331,527 and Canadian Patent No. 2,148,954. Patents such as U.S. Patent Nos. 5,521,128 and 5,346,867 to Jones, et al. and 5,411,922 to Jones further includes manganese and/or titanium. Still, other glasses may include

SDOCID: <WO___9958462A2_I_>

additional materials, such as disclosed in WO 96/00194, which teaches the inclusion of fluorine, zirconium, zinc, cerium, titanium and copper in the glass composition and requires that the sum of the alkaline earth oxides be less than 10 weight percent of the glass.

One particular blue composition that provides superior spectral performance is disclosed in U.S. Patent No. 4,792,536 to Pecoraro, et al. Commercial products which incorporate this patent are sold by PPG Industries, Inc. under the trademarks SOLEXTRA® and AZURLITE®. This glass has a dominant wavelength ranging from about 486 to 489 nm and excitation purity ranges from about 8 to 14 percent. It would be advantageous to be able to produce a dark tinted blue colored glass to complement this blue colored glass using conventional glass melting processing techniques.

SUMMARY OF THE INVENTION

The present invention provides a blue colored, infrared and ultraviolet absorbing glass composition having a luminous transmittance of up to 60 percent. The glass uses a standard soda-lime-silica glass base composition and additionally iron and cobalt, and optionally selenium and/or titanium, as infrared and ultraviolet radiation absorbing materials and colorants. The glass of the present invention has a color characterized by a dominant wavelength in the range of 480 to 489 nanometers and an excitation purity of at least 8 percent at a thickness of 0.160 inches (4.06 millimeters).

In one embodiment of the invention, the glass composition of a blue colored, infrared and ultraviolet radiation absorbing soda-lime-silica glass article includes a solar radiation absorbing and colorant portion consisting essentially of 0.9 to 2.0 percent by weight total iron, 0.15 to 0.65 percent by weight FeO, 90 to 250 PPM CoO, and optionally up to 12 PPM Se and up to 0.9 wt% TiO₂, and preferably 1 to 1.4 percent by weight total iron, 0.20 to 0.50

Butter the state of the second

5

15

percent by weight FeO, 100 to 150 PPM CoO, up to 8 PPM Se, and up to 0.5 wt% TiO₂.

DETAILED DESCRIPTION OF THE INVENTION

The base glass of the present invention, that is, the major constituents of the glass without infrared or ultraviolet absorbing materials and/or colorants, which are an object of the present invention, is commercial sodalime-silica glass typically characterized as follows:

	Weight Percent
10	SiO ₂ 66 to 75
	Na ₂ O 10 to 20
	CaO 5 to 15
电线 医电路电流	MgO 0 to 5
	Al ₂ O ₃ 0 to 5
15	K ₂ O 0 to 5

As used herein, all "weight percent (wt%)" values are based on the total weight of the final glass composition.

To this base glass, the present invention adds infrared and ultraviolet radiation absorbing materials and colorants in the form of iron and cobalt and optionally selenium and/or titanium. As disclosed herein with respect to the glass compositions, iron is expressed in terms of Fe₂O₃ and FeO, cobalt is respected in terms of CoO, selenium is expressed in terms of elemental Se and titanium is expressed in terms of TiO₂. It should be appreciated that the glass compositions disclosed herein may include small amounts of other materials, for example, melting and refining aids, tramp materials or impurities. It should be further appreciated that in one embodiment of the invention, small amounts of additional materials may be included in the glass to provide the desired color characteristics and improve the solar performance of the glass, as will be discussed later in more detail.

Commence We will take

The iron oxides in a glass composition perform several functions. Ferric oxide, Fe_2O_3 , is a strong ultraviolet radiation absorber and operates as a yellow colorant in the glass. Ferrous oxide, FeO, is a strong infrared radiation absorber and operates as a blue colorant. The total amount of iron present in the glasses disclosed herein is expressed in terms of Fe_2O_3 in accordance with standard analytical practice but that does not imply that all of the iron is actually in the form of Fe_2O_3 . Likewise, the amount of iron in the ferrous state is reported as FeO even though it may not actually be present in the glass as FeO. In order to reflect the relative amounts of ferrous and ferric iron in the glass compositions disclosed herein, the term "redox" shall mean the amount of iron in the ferrous state (expressed as FeO) divided by the amount of total iron (expressed as Fe_2O_3). Furthermore, unless stated otherwise, the term "total iron" in this specification shall mean total iron expressed in terms of Fe_2O_3 and the term "FeO" shall mean iron in the ferrous state expressed in terms of FeO.

CoO operates as a blue colorant and does not exhibit any appreciable infrared or ultraviolet radiation absorbing properties. Se is an ultraviolet absorbing colorant that imparts a pink or brown color to soda-lime-silica glass. Se may also absorb some infrared radiation and its use tends to reduce redox. TiO₂ is an ultraviolet radiation absorber that operates as a colorant imparting a vellow color to the glass composition. A proper balance between the iron, i.e. ferric and ferrous oxides and cobalt, and optionally selenium and/or titanium is required to obtain the desired blue colored privacy glass with the desired spectral properties.

The glass of the present invention may be melted and refined in a continuous, large-scale, commercial glass melting operation and formed into flat glass sheets of varying thickness by the float process in which the molten glass is supported on a pool of molten metal, usually tin, as it assumes a ribbon shape and is cooled, in a manner well known in the art.

Although it is preferred that the glass disclosed herein be made using a conventional, overhead fired continuous melting operation, as is well known in the art, the glass may also be produced using a multi-stage melting operation, as disclosed in U.S. Patent Nos. 4,381,934 to Kunkle, et al., 4,792,536 to Pecoraro, et al. and 4,886,539 to Cerutti, et al. If required, a stirring arrangement may be employed within the melting and/or forming stages of the glass production operation to homogenize the glass in order to produce glass of the highest optical quality.

Depending on the type of melting operation, sulfur may be added to the batch materials of a soda-lime-silica glass as a melting and refining aid. 10 Commercially produced float glass may include up to about 0.3 wt% SO₃. In a glass composition that includes iron and sulfur, providing reducing conditions may create amber coloration which lowers luminous transmittance as discussed in U.S. Patent No. 4,792,536 to Pecoraro, et al. However, it is believed that the reducing conditions required to produce this coloration in float glass compositions of the type disclosed herein are limited to approximately the first 20 microns of the lower glass surface contacting the molten tin during the float forming operation, and to a lesser extent, to the exposed upper glass surface. Because of the glass' low sulfur content and the limited region of the glass in which any coloration could occur, depending on the particular soda-lime-silica-glass composition, sulfur in these surfaces essentially has no material effect on the glass color or spectral properties.

It should be appreciated that as a result of forming the glass on molten tin as discussed above, measurable amounts of tin oxide may migrate into 25 surface portions of the glass on the side contacting the molten tin. Typically, a piece of float glass has an SnO₂ concentration ranging from about 0.05 to 2 wt% in about the first 25 microns below the surface of the glass that was in contact with the tin. Typical background levels of SnO₂ may be as high as 30 parts per million (PPM). It is believed that high tin concentrations in about the

15

a commence of the and the

first 10 angstroms of the glass surface supported by the molten tin may slightly increase the reflectivity of that glass surface; however, the overall impact on the glass properties is minimal.

Table 1 illustrates examples of experimental glass melts having glass compositions which embody the principles of the present invention. Similarly, Table 2 illustrates a series of computer modeled glass compositions embodying the principles of the present invention. The modeled compositions were generated by a glass color and spectral performance computer model developed by PPG Industries, Inc. Tables 1 and 2 list only the iron, cobalt, selenium and titanium portions of the examples. Analysis of selected experimental melts in Table 1 indicates that it is expected that the melts would most likely include up to about 10 PPM Cr₂O₃ and up to about 39 PPM MnO₂. Examples 5-19 also included up to about 0.032 weight percent TiO₂. It is presumed that the Cr₂O₃, MnO₂ and TiO₂ entered the glass melts as part of the cullet. In addition, the modeled compositions were modeled to include 7 PPM Cr₂O₃. It is believed that glass compositions of the instant invention produced by a commercial float process as discussed earlier may include low levels of Cr₂O₃ and MnO₂ and less than 0.020 weight percent TiO₂, but these levels of such materials are considered to be tramps levels which would not materially affect the color characteristics and spectral properties of the blue glass of the present invention.

The spectral properties shown for Tables 1 and 2 are based on a reference thickness of 0.160 inches (4.06 mm). It should be appreciated that the spectral properties of the examples may be approximated at different thicknesses using the formulas disclosed in U.S. Patent No. 4,792,536.

With respect to the transmittance data provided in Table 1, the luminous transmittance (LTA) is measured using C.I.E. standard illuminant "A" with a 2° observer over the wavelength range of 380 to 770 nanometers. Glass color, in terms of dominant wavelength and excitation purity, is

10

20

measured using C.I.E. standard illuminant "C" with a 2° observer, following the procedures established in ASTM E308-90. The total solar ultraviolet transmittance (TSUV) is measured over the wavelength range of 300 to 400 nanometers, total solar infrared transmittance (TSIR) is measured over the wavelength range of 720 to 2000 nanometers, and total solar energy transmittance (TSET) is measured over the wavelength range of 300 to 2000 nanometers. The TSUV, TSIR and TSET transmittance data are calculated using Parry Moon air mass 2.0 direct solar irradiance data and integrated using the Trapezoidal Rule, as is known in the art. The spectral properties presented in Table 2 are based on the same wavelength ranges and calculation procedures.

Sample Preparation

The information provided for Examples 1-4 in Table 1 is based on

experimental laboratory melts having approximately the following batch
components:

	cullet A	<u>Ex. 1-3</u> 3000 gm	2850 gm
	cullet B		150 gm
20	TiO ₂	6 am	6 gm

Cullet A included about 1.097 wt% total iron, 108 PPM CoO, 12 PPM Se and 7 PPM Cr₂O₃. Cullet B included about 0.385 wt% total iron, 67 PPM CoO, 12 PPM Se and 8 PPM Cr₂O₃. In preparing the melts, the ingredients were weighed out, mixed, placed in a platinum crucible and heated to 2650°F (1454°C) for 2 hours. Next, the molten glass was fritted in water, dried and reheated to 2650°F (1454°C) in a platinum crucible for 1 hour. The molten glass was then fritted a second time in water, dried and reheated to 2650°F (1454°C) in a platinum crucible for 2 hours. The molten glass was then

- 8 -

poured out of the crucible to form a slab and annealed. Samples were cut from the slab and ground and polished for analysis.

The information provided for Examples 5-19 in Table 1 is based on experimental laboratory melts having approximately the following batch components:

cullet	239.74 gm
sand	331.10 gm
soda ash	108.27 gm
limestone	28.14 gm
dolomite	79.80 gm
salt cake	2.32 gm
Fe ₂ O ₃ (total iron)	as required
Co ₃ O ₄	as required
Se	as required
TiO ₂	as required

The raw materials were adjusted to produce a final glass weight of 700 grams. Reducing agents were added as required to control redox. The cullet used in the melts (which formed approximately 30% of the melt) included up to 0.51 wt% total iron, 0.055 wt% TiO₂ and 7 PPM Cr₂O₃. In preparing the melts, the ingredients were weighed out and mixed. A portion of the raw batch material was then placed in a silica crucible and heatened to 2450°F (1343°C). When the batch material melted down, the remaining raw materials were added to the crucible and the crucible was held at 2450°F (1343°C) for 30 minutes. The molten batch was then heated and held at temperatures of 2500°F (1371°C). 2550°F (1399°C), 2600°F (1427°C) for 30 minutes, 30 minutes and 1 hour, respectively. Next, the molten glass was fritted in water, dried and reheated to 2650°F (1454°C) in a platinum crucible for two hours. The molten glass was then poured out of the crucible to form a slab and

al Adaption and the state of the state of

10

annealed. Samples were cut from the slab and ground and polished for analysis.

The chemical analysis of the glass compositions (except for FeO) was determined using a RIGAKU 3370 X-ray fluorescence spectrophotometer.

5 The spectral characteristics of the glass were determined on annealed samples using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer prior to tempering the glass or prolonged exposure to ultraviolet radiation, which will effect the spectral properties of the glass. The FeO content and redox were determined using the glass color and spectral performance computer model developed by PPG Industries, Inc.

The following is the approximate basic oxides of the experimental melts disclosed in Table 1:

		Ex. 1-3	<u>Ex. 4</u>	Ex. 5-19	• •
	SiO ₂ (wt%)	66.1	66.8	72.4	
15	Na ₂ O (wt%)	17.8	17.4	13.5	
	CaO (wt%)	7.8	7.9	8.7	
	MgO (wt%)	3.1	3.1	3.7	
	Al2O3 (wt%)	3.1	2.8	0.17	
	K ₂ O (wt%)	0.70	0.63	0.049	

20 It is expected that the basic oxide constituents of commercial soda-lime-silica glass compositions based on the experimental melts disclosed in Table 1 and the modeled compositions disclosed in Table 2 would fall within the ranges of the glass constituents as discussed earlier.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
Total iron (wt%)	1.110	1.116	1.117	1.044	1.233	1.230	1.237	1.238	1.236	1.232
FeO (wt%)	0.389	986.0	0.394	0.379	0.317	0.316	0.329	0.317	0.304	0.320
Model redox	0.350	0.346	0.353	0.362		0.257	0.266	0.256	0.246	0.260
CoO (PPM)	134	129	131	128	18	128	127	126	116	126
Se (PPM)	ļ.	10		11	9	7	5	9	8	9
TiO ₂ (wt%)	0.199	0.188	0.188	0.173	0.020	0.021	0.020	0.021	0.022	0.020
LTA (%)	28.1.	28.8	29.5	29.6	35.1	35.2	35.4	35.4	35.7	35.8
TSUV (%)	16.6	17.0	18.1	19.1	21.7	21.4	22.0	21.6	20.4	22.12
TSIR (%)	9.5	9.2	8.9	9.7	12.7	13.9	11.9	12.7	13.7	12.4
TSET (%)	18.0	18.4	18.6	19.1	24.5	25.2	24.3	24.7	25.1	24.8
DW (nm)	486.6	488.5	487.7	488.0	484.9	485.1	484.7	485.0	487.0	484.7
Pe (%)	9.8	10.0	11.1	9.5	13.0	12.0	14.4	13.2	8.9	13.7
				-					3.	

	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	
Total iron (wt%)	1.234	1.225	1.226	1.204	1.212	1.217	1.208	1.213	1.204	
FeO (wt%)	0.313	0.296	0.318	0.384	0.325	0.323	0.315	0.312	0.307	
Model redox	0.254	0.242	0.259	0.319	0.268	0.265	0.261	0.257	0.255	
CoO (PPM)	126	124	126	91	63	92	94	94	90	
Se (PPM)	5	9	9	0	0	0	0	0	0	
TiO ₂ (wt%)	0.022	0.019	0.020	0.024	0.029	0.032	0.032	0.032	0.028	
LTA (%)	36.2	36.3	36.4	44.7	45.4	45.4	45.5	45.6	46.7	
TSUV (%)	22.3	21.7	22.5	29.3	27.7	27.4	27.3	27.2	27.8	
TSIR (%)	12.9	14.3	12.7	8.5	11.9	12.3	12.8	13.0	13.3	
TSET (%)	25.2	26.0	25.2	26.9	29.0	29.1	29.5	29.7	30.3	
DW (nm)	484.7	485.0	484.6	484.8	484.9	484.9	484.9	484.9	485.2	
Pe (%)	13.8	12.8	14.3	18.0	17.0	16.9	16.5	16.7	16.1	
								-		

.*	•	-5 ·*.						· .						·	.'		<u> </u>			_	· ·		- 1			
Ex. 28	1.1	0.33	0.3	110	10	0.02	35.5	24.2	12.7	23.6	485.2	9.9		Ex. 37	1.1	0.24	0.22	140	က	0.05	38.9	26.1	20.9	30.5	482.9	17.4
Ex. 27	1.1	0.17	0.15	200	0	0	35.1	25.9	32.7	36.1	480.5	25.2		Ex. 36	1.8	0.40	0.22	110	-	0.02	38.5	16.3	8.9	22.5	488.6	15.4
Ex. 26	1.1	0.17	0.15	200	0	0.05	35.0	25.4	32.7	36.0	480.6	24.8		Ex. 35	1.3	0.29	0.22	140	3	0.02	37.1	22.4	16.3	56.9	484.1	17.3
Ex. 25	0.975	0.23	0.24	190	0	0.1	35.0	30.8	21.8	30.7	480.1	27.9		Ex. 34	1.6	0.35	0.22	140	1	0.02	36.1	18.8	11.3	23.5	485.3	19.4
Ex. 24	1.3	0.46	0.35	140	0	0.4	34.9	25.5	6.5	21.1	483.0	25.9		Ex. 33	11	0.39	0.35	95	10	0.02	36.1	25.9	9.4	22.0	485.5	10.6
Ex. 23	1.45	0.51	0.35	150	0	9.0	31.8	21.7	4.9	18.6	483.4	26.6		Ex. 32	1.2	0.31	0.26	150	1	9.0	36.0	21.8	14.1	25.2	484.0	19.0
Ex. 22	16	0.56	0.35	175	0	9.0	27.8	19.7	2.8	16.3	482.7	30.5		Ex. 31		0.31	0.28	110	2	0.02	36.0	23.6	14.4	24.6	485.7	8.7
Fx 21		0.63	0.35	200	0	0	24.8	21.5	2.7	15.2	4811	38.4		Fx 30	1 45	0.32	0.22	140	3	0.05	35.9	20.0	13.5	24.6	485.0	17.3
Fy 20		0.63	0.35	200	C	90	23.9	17.4	2.7	141	482 1	34.5		FV 29	10	0.22	0.22	175		0.4	35.9	25.8	23.7	31.1	481.5	21.7
	(20th) nori leto	Foldings (wt/0)	Model redox	Mod/ Co	Se (DPM)	TiOn (wt%)	QZ (W(.0)	(%) (%)	TSIR (%)	SET (%)	(v) (v)	Do (%)	(2/)		(%) trop (1410%)		odel redox	CoO (PPM)	Se (PPM)	(wt%)	1 TA (%)	(%) (113	TSID (%)	TOET (%)	13E1 (70)	Pe (%)
٠.	F	ــا اـــ	≥ا≥	٤١٥	ن [د	Ďμ		٦Į٢	- ř	<u> </u>	- [واد			E	<u>- [u</u>	_ ≥	≥ اد) <i>(</i> 7.	١F	<u>: -</u>	1 ⊢	<u>- F</u>	<u>- </u>	<u>-1</u> ⊆	10

1911年1946年 美国中华大学

TABLE 2 (cont'd.)

*		<u> 12-</u> 5	11.									
Ex. 44	1.0	0.25	0.25	6	0	0	50.1	32.1	20.1	34.9	484.9	15.3
Ex. 43	1.0	0.22	0.22	95	0	0.02	50.1	30.7	23.9	36.9	485.0	14.3
Ex. 42	1.0	0.22	0.22	110	0	0.02	47.4	30.7	23.9	36.0	483.9	16.4
Ex. 41	1.0	0.22	0.22	120	0	0.05	45.6	30.3	23.8	35.3	483.4	17.6
Ex. 40	1.	0.28	0.25	110	0	0	45.3	30.0	17.4	31.5	484.0	18.2
Ex. 39	1.1	0.31	0.28	130	0	0.1	41.0	29.6	14.4	28.4	482.8	21.9
Ex. 38	1.1	0.28	0.25	140	3		40.6	29.6	17.4	30.0	482.4	22.4
	Total iron (wt%)	FeO (wt%)	Model redox	CoO (PPM)	Se (PPM)	TiO ₂ (wt%)	LTA (%)	TSUV (%)	TSIR (%)	TSET (%)	DW (nm)	Pe (%)

15

SDOCID: <WO _ 9958462A2_I_>

Referring to Tables 1 and 2, the present invention provides a blue colored glass having a standard soda-lime-silica glass base composition and additionally iron and cobalt, and optionally selenium and titanium, as infrared and ultraviolet radiation absorbing materials and colorants, a luminous transmittance (LTA) of greater than 20% up to 60%, and a color characterized by a dominant wavelength (DW) in the range of 480 to 489 nanometers (nm), preferably 482 to 487 nm, and an excitation purity (Pe) of at least 8%, preferably 10 to 30% at a thickness of 0.16 inches (4.06 mm). It is anticipated that the color of the glass may vary within the dominant wavelength range to provide a desired product.

The redox ratio for the glass is maintained between 0.15 to 0.40, preferably between 0.20 to 0.35, more preferably between 0.24 to 0.32. The glass composition also has a TSUV of no greater than 35%, preferably no greater than 30%; a TSIR of no greater than 25%, preferably no greater than 20%; and a TSET of no greater than 40%, preferably no greater than 35%.

In one particular embodiment, the glass composition includes 0.9 to 2 wt% total iron, preferably 1 to 1.4 wt% total iron, and more preferably 1.1 to 1.3 wt% total iron; 0.15 to 0.65 wt% FeO, preferably 0.2 to 0.5 wt% FeO, and more preferably 0.24 to 0.40 wt% FeO; and 90 to 250 PPM CoO, preferably 100 to 150 PPM CoO, and more preferably 110 to 140 PPM CoO. As discussed earlier, selenium may also be included in the glass composition and more specifically, 0 to 12 PPM Se, preferably 0 to 8 PPM Se. One embodiment of the invention includes 1 to 6 PPM Se. Similarly, titanium may also be included in the glass composition, and more specifically, 0 to 0.9 wt% TiO₂, preferably, 0 to 0.5 wt % TiO₂. One embodiment of the invention includes 0.02 to 0.3 wt% TiO₂.

In one particular embodiment of the invention, the glass composition is selenium-free and has an LTA of greater than 20% up to 60%, and preferably greater than 35% up to 55%. In another embodiment of the

المال المال ما المالية والمعروب المعروب المالية

5

15

20

25

invention, the glass composition is selenium-free and has less than 200 PPM CoO. In still another embodiment of the invention, the glass composition has up to 12 PPM Se and has an LTA of greater than 35% up to 60%, preferably 40 to 55%.

It is expected that the spectral properties of the glass will change after tempering the glass and further upon prolonged exposure to ultraviolet radiation, commonly referred to as "solarization". In particular, it is estimated that tempering and solarization of the glass compositions disclosed herein may reduce the LTA and TSIR by about 0.5 to 1%, reduce the TSUV by about 1 to 2%, and the TSET by about 1 to 1.5%. As a result, in one embodiment of the invention, the glass has selected spectral properties that initially fall outside the desired ranges previously discussed but fall within the desired ranges after tempering and/or solarization.

Glass as disclosed herein and made by the float process typically ranges from a sheet thickness of about 1 millimeter to 10 millimeters.

For vehicle glazing applications, it is preferred that the glass sheets having a composition and spectral properties as disclosed herein have a thickness within the range of 0.121 to 0.197 inches (3.1 to 5 mm). It is anticipated that when using a single glass ply in the above thickness range, the glass will be tempered, e.g. for an automotive side or rear window.

It is also contemplated that the glass will have architectural applications and be used at thicknesses ranging from about 0.14 to 0.24 inches (3.6 to 6 mm).

When multiple plies are used for either automotive or architectural applications, it is anticipated that the glass plies will be annealed and laminated together using a thermoplastic adhesive, such as polyvinyl butyral.

As discussed earlier, other materials may also be added to the glass compositions disclosed herein to further reduce infrared and ultraviolet

radiation transmission and/or control glass color. In particular, it is contemplated that the following materials may be added to the iron and cobalt, and optionally selenium and/or titanium containing soda-lime-silica glass disclosed herein:

5	Nd ₂ O ₃	0 to 1 wt%
	SnO ₂	0 to 2 wt%
	ZnO	0 to 1 wt%
	MoO ₃	0 to 0.03 wt%
	CeO ₂	0 to 2 wt%
10	NiO	0 to 0.1 wt%

As should be appreciated, adjustments may have to be made to the basic iron, cobalt, selenium and titanium constituents to account for any coloring and/or redox affecting power of these additional materials.

Other variations as are known to those skilled in the art may be
15 resorted to without departing from the scope of the invention as defined by
the claims that follow.

WE CLAIM:

10

15

25

1. A blue colored, infrared and ultraviolet radiation absorbing glass composition having a composition comprising a base glass portion comprising:

	SiO ₂	66 to 75 percent by weight,
	Na₂O	10 to 20 percent by weight,
	CaO	5 to 15 percent by weight,
	MgO	0 to 5 percent by weight,
	Al ₂ O ₃	0 to 5 percent by weight,
	K₂O	0 to 5 percent by weight,
and a sola	r radiation ab	sorbing and colorant portion consisting essentially
of:		(영화) 등 전 경험 시간 (1985년) 경험 (1985년) (1985년) (1985년) (1985년) 1987년 - 1987년 (1985년) (1985년

total iron 0.9 to 2 percent by weight,

FeO 0.15 to 0.65 percent by weight,

CoO 90 to 250 PPM, and

TiO₂ 0 to 0.9 percent by weight,

the glass having a luminous transmittance (LTA) of greater than 20% up to 60%, and a color characterized by a dominant wavelength in the range of 480 to 489 nanometers and an excitation purity of at least 8% at a thickness of 0.160 inches.

- 2. The composition as in claim 1 wherein the total iron concentration is from 1 to 1.4 weight percent, the FeO concentration is 0.20 to 0.50 weight percent, the CoO concentration is 100 to 150 PPM, and the TiO₂ concentration is 0 to 0.5 weight percent.
 - 3. The composition as in claim 2 wherein the composition has a redox of 0.20 to 0.35.

- 4. The composition as in claim 2 wherein the total iron concentration is from 1.1 to 1.3 weight percent, the FeO concentration is 0.24 to 0.40 weight percent, and the CoO concentration is 110 to 140 PPM.
- 5. The composition as in claim 4 wherein the ${\rm TiO_2}$ concentration is 0.02 to 0.40 weight percent.
- 6. The composition as in claim 4 wherein the glass has a total solar ultraviolet transmittance (TSUV) of 35 percent or less, a total solar infrared transmittance (TSIR) of 25 percent or less and a total solar energy (TSET) transmittance of 40 percent or less, and the color of the glass is characterized by a dominant wavelength in the range of 482 to 487 nanometers and an excitation purity of 10 to 30 percent at a thickness of 0.160 inches.
 - 7. The composition as in claim 6 wherein the glass has a total solar ultraviolet transmittance (TSUV) of 30 percent or less, a total solar infrared transmittance (TSIR) of 20 percent or less and a total solar energy transmittance (TSET) of 35 percent or less at a thickness of 0.160 inches.
 - 8. The composition as in claim 6 wherein the glass has a luminous transmittance (LTA) of greater than 35 up to 55 percent.
- 9. The composition as in claim 1 wherein the glass has a total solar ultraviolet transmittance (TSUV) of 35 percent or less, a total solar infrared transmittance (TSIR) of 25 percent or less and a total solar energy transmittance (TSET) of 40 percent or less at a thickness of 0.160 inches.

- 10. The composition as in claim 1 wherein the glass has a luminous transmittance (LTA) of greater than 35 up to 55 percent.
- 11. The composition as in claim 1 wherein the color of the glass is characterized by a dominant wavelength in the range of 482 to 489 nanometers and an excitation purity of 10 to 30 percent.
 - 12. The composition as in claim 1 wherein the composition has a redox of 0.15 to 0.40.
 - 13. A flat glass sheet formed by the float process from the glass composition recited in claim 1.
- 14. An automotive window formed from the flat glass sheet of15 claim 13.
 - 15. A blue colored, infrared and ultraviolet radiation absorbing glass composition having a composition comprising a base glass portion comprising:

20

25

10

SiO₂ 66 to 75 percent by weight, Na₂O 10 to 20 percent by weight,

CaO 5 to 15 percent by weight,

MgO 0 to 5 percent by weight,

Al₂O₃ 0 to 5 percent by weight,

K₂O 0 to 5 percent by weight,

and a solar radiation absorbing and colorant portion consisting essentially of:

total iron 0.9 to 2 percent by weight,

FeO 0.15 to 0.65 perce. by weight,

CoO 90 to less than 200 PPM, and

TiO₂ 0 to 0.9 percent by weight

the glass having a luminous transmittance (LTA) of up to 60 percent, and the color of the glass characterized by a dominant wavelength in the range of 480 to 489 nanometers and an excitation purity of at least 8 percent at a thickness of 0.160 inches.

- 16. The composition as in claim 15 wherein the glass has a luminous transmittance (LTA) of greater than 20 percent up to 55 percent, a total solar ultraviolet transmittance (TSUV) of 35 percent or less, a total solar infrared transmittance (TSIR) of 25 percent or less and a total solar energy (TSET) transmittance of 40 percent or less, and the color of the glass is characterized by a dominant wavelength in the range of 482 to 489 nanometers and an excitation purity of 10 to 30 percent at a thickness of 0.160 inches.
 - 17. A blue colored, infrared and ultraviolet radiation absorbing glass composition having a composition comprising a base glass portion comprising:

SiO₂ 66 to 75 percent by weight,
Na₂O 10 to 20 percent by weight,
CaO 5 to 15 percent by weight,
MgO 0 to 5 percent by weight,
Al₂O₃ 0 to 5 percent by weight,

SiO₂ 66 to 75 percent by weight,
O to 5 percent by weight,
O to 5 percent by weight,
O to 5 percent by weight,

and a solar radiation absorbing and colorant portion consisting essentially of:

total iron 0.9 to 2 percent by weight,

FeO 0.15 to 0.65 percent by weight,

CoO 90 to 250 PPM,

TiO₂

Se 0 to 12 PPM, and

the glass having a luminous transmittance (LTA) of greater than 35% up to 60 percent, and the color of the glass characterized by a dominant wavelength in the range of 480 to 489 nanometers and an excitation purity

0 to 0.9 percent by weight

of at least 8 percent at a thickness of 0.160 inches.

18. The composition as in claim 17 wherein the total iron
10 concentration is from 1 to 1.4 weight percent, the FeO concentration is 0.20 to 0.50 weight percent, the CoO concentration is 100 to 150 PPM, the Se concentration is 0 to 8 PPM, and the TiO₂ concentration is 0 to 0.5 weight percent.

- 15 19. The composition as in claim 18 wherein the composition has a redox of 0.20 to 0.35.
 - 20. The composition as in claim 18 wherein the total iron concentration is from 1.1 to 1.3 weight percent, the FeO concentration is 0.24 to 0.40 weight percent, and the CoO concentration is 110 to 140 PPM.
 - 21. The composition as in claim 20 wherein the TiO₂ concentration is from 0.02 to 0.40 weight percent.
- 25 The composition as in claim 20 wherein the Se concentration is from 1 to 6 PPM.
 - 23. The composition as in claim 20 wherein the glass has a total solar ultraviolet transmittacre (TSUV) of 35 percent or less, a total solar

infrared transmittance (TSIR) of 25 percent or less and a total solar energy (TSET) transmittance of 40 percent or less, and the color of the glass is characterized by a dominant wavelength in the range of 482 to 487 nanometers and an excitation purity of 10 to 30 percent at a thickness of 0.160 inches.

- 24. The composition as in claim 23 wherein the glass has a total solar ultraviolet transmittance (TSUV) of 30 percent or less, a total solar infrared transmittance (TSIR) of 20 percent or less and a total solar energy transmittance (TSET) of 35 percent or less at a thickness of 0.160 inches.
- 25. The composition as in claim 23 wherein the glass has a luminous transmittance (LTA) of 40 to 55 percent.

To the contract of

- 15 26. The composition as in claim 17 wherein the glass has a total solar ultraviolet transmittance (TSUV) of 35 percent or less, a total solar infrared transmittance (TSIR) of 25 percent or less and a total solar energy transmittance (TSET) of 40 percent or less at a thickness of 0.160 inches
- 27. The composition as in claim 17 wherein the glass has a luminous transmittance (LTA) of 40 to 55 percent.
- 28. The composition as in claim 17 wherein the color of the glass is characterized by a dominant wavelength in the range of 482 to 489 nanometers and an excitation purity of 10 to 30 percent.
 - 29. The composition as in claim 17 wherein the composition has a redox of 0.15 to 0.40.

- 30. A flat glass sheet formed by the float process from the glass composition recited in claim 17.
- 31. An automotive window formed from the flat glass sheet of 5 claim 30.
 - 32. A blue colored, infrared and ultraviolet radiation absorbing glass composition having a composition comprising a base glass portion comprising:

10 SiO₂ 66 to 75 percent by weight,

Na₂O 10 to 20 percent by weight,

CaO 5 to 15 percent by weight,

MgO 0 to 5 percent by weight,

Al₂O₃ 0 to 5 percent by weight,

K₂O 0 to 5 percent by weight,

and a solar radiation absorbing and colorant portion consisting essentially

and a solar radiation absorbing and colorant portion consisting essentially of:

0.9 to 2 percent by weight, total iron 0.15 to 0.65 percent by weight, FeO 90 to 250 PPM. 20 CoO 0 to 12 PPM Se TiO₂ 0 to 0.9 percent by weight, 0 to 1 percent by weight, Nd_2O_3 SnO₂ 0 to 2 percent by weight, 25 ZnO 0 to 1 percent by weight, 0 to 0.03 percent by weight, MoO₃ 0 to 2 percent by weight, and CeO₂ NiO 0 to 0.1 percent by weight,

the glass having a luminous transmittance (LTA) of greater than 35 percent up to 60 percent, and the color of the glass characterized by a dominant wavelength in the range of 480 to 489 nanometers and an excitation purity of at least 8 percent at a thickness of 0.160 inches.

5

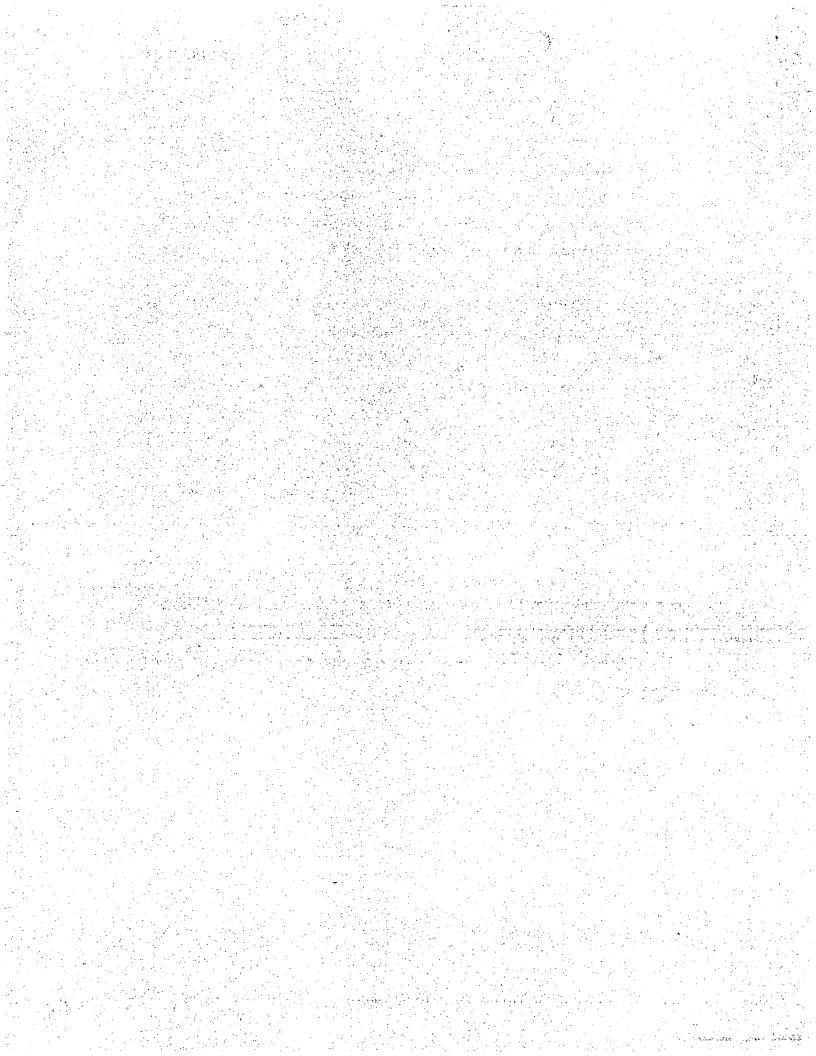
33. The composition as in claim 32 wherein the glass has a total solar ultraviolet transmittance (TSUV) of 35 percent or less, a total solar infrared transmittance (TSIR) of 25 percent or less and a total solar energy transmittance (TSET) of 40 percent or less at a thickness of 0.160 inches.

10

34. The composition as in claim 33 wherein the color of the glass is characterized by a dominant wavelength in the range of 482 to 487 nanometers and an excitation purity of 10 to 30 percent at a thickness of 0.160 inches.

15

- 35. The composition as in claim 34 wherein the total iron concentration is from 1.0 to 1.4 weight percent, the FeO concentration is 0.2 to 0.5 weight percent, the CoO concentration is 100 to 150 PPM, the Se concentration is 0 to 8 PPM, and the TiO₂ concentration is 0 to 0.50 weight percent.
- 36. A flat glass sheet formed by the float process from the glass composition recited in claim 35.



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:	3	(11) International Publication Number: WO 99/58462
C03C 3/087, 4/02, 4/08	A3	(43) Internati nal Publication Date: 18 November 1999 (18.11.99)

US

(21) International Application Number: PCT/US99/10295 (81) Designate BY, C
(22) International Filing Date: 11 May 1999 (11.05.99) GE, C

12 May 1998 (12.05.98)

(71) Applicant: PPG INDUSTRIES OHIO, INC. [US/US]; 3800

West 143rd Street, Cleveland, OH 44111 (US).

(72) Inventors: KRUMWIEDE, John, F.; 315 Blue Run Road, Cheswick, PA 15024 (US). SHELESTAK, Larry, J.; 1046 Ford Street, P.O. Box 233, Bairdford, PA 15006 (US).

(74) Agents: STACHEL, Kenneth, J.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al. (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(88) Date of publication of the international search report: 20 January 2000 (20.01.00)

(54) Title: BLUE PRIVACY GLASS

(57) Abstract

(30) Priority Data:

09/076,566

The present invention provides a blue colored, infrared and ultraviolet absorbing glass composition having a luminous transmittance of up to 60 percent. The glass uses a standard soda-lime-silica glass base composition and additionally iron and cobalt, and optionally selenium and/or titanium, as infrared and ultraviolet radiation absorbing materials and colorants. The glass of the present invention has a color characterized by a dominant wavelength in the range of 480 to 489 nanometers and an excitation purity of at least 8 percent at a thickness of 0.160 inches (4.06 millimeters). In one embodiment of the invention, the glass composition of a blue colored, infrared and ultraviolet radiation absorbing soda-lime-silica glass article includes a solar radiation absorbing and colorant portion consisting essentially of 0.9 to 2.0 percent by weight total iron, 0.15 to 0.65 percent by weight FeO, 90 to 250 PPM CoO, and optionally up to 12 PPM Se and up to 0.9 wt.% TiO₂, and preferably 1 to 1.4 percent by weight total iron, 0.20 to 0.5 percent by weight FeO, 100 to 150 PPM CoO, up to 8 PPM Se, and up to 0.5 wt.% TiO₂.

FOR THE PURPOSES OF INFORMATION ONLY.

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM ·	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA -	Gabon	LV	Latvia	SZ	Swaziland
ΑZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB -	Barbados	GH .	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	A 10	Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL.	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW'	Malawi	US	United States of America
CA	Canada	IT	Italy	MX .	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
· CG	Congo	KE .	Kenya	NL	Netherlands	YU	Yugoslavia
СН	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW .	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	"NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal	7 7 6 6 7	
CU	Cuba	KZ	Kazakstan	RO 📑	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation	11.	
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE.	Estonia	LR	Liberia	SG	Singapore		

SDOCID: <WO___9958462A3_I_>

INTERN IONAL SEARCH REPORT

International Application No Pc./US 99/10295

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C3/087 C03C4/02 C03C4/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
P,X	EP 0 887 320 A (GLAVERBEL) 30 December 1998 (1998-12-30) examples 9,13,23,46,48,91	1-36		
P,X	US 5 851 940 A (BOULOS EDWARD NASHED ET AL) 22 December 1998 (1998-12-22) examples 28-31	1-36		
P, X	US 5 807 417 A (BOULOS EDWARD NASHED ET AL) 15 September 1998 (1998-09-15) examples 28-31	1-36		
X	EP 0 536 049 A (SAINT GOBAIN VITRAGE) 7 April 1993 (1993-04-07) examples 1,2,4,5,7-11,13	1-36		
		244		

Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance.	'T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filling date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filling date but later than the priority date claimed	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search 17 November 1999	Date of mailing of the international search report 23/11/1999
17 NOVERIDER 1333	I

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNA NAL SEARCH REPORT

International Application No. PC1/US 99/10295

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT					
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.			
X	WO 96 00194 A (SAINT GOBAIN VITRAGE; COMBES JEAN MARIE (FR); MAZON RAMOS PEDRO PA) 4 January 1996 (1996-01-04) cited in the application examples 8,9	1-36			
	US 5 393 593 A (GULOTTA JOSEPH A ET AL) 28 February 1995 (1995-02-28) cited in the application example 11 tables I,II	1-36			
	EP 0 705 800 A (ASAHI GLASS CO LTD) 10 April 1996 (1996-04-10) cited in the application examples 2,8,10	1-36			

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNA ONAL SEARCH REPORT

nformation on patent family members

PC., US 99/10295

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
EP 0887320 A	30-12-1998	LU	90084 A	28-12-1998
		CZ	9802032 A	13-01-1999
		JP	11071131 A	16-03-1999
		PL	327003 A	04-01-1999
US 5851940 A	22-12-1998	WO	9902461 A	21-01-1999
US 5807417 A	15-09-1998	WO	9902462 A	21-01-1999
EP 0536049 A	07-04-1993	FR	2682101 A	09-04-1993
		AT	156103 T	15-08-1997
		CA	2097189 A	04-04-1993
		CZ	9301210 A	18-05-1994
		DE	69221244 D	04-09-1997
		DE	69221244 T	19-03-1998
		DK.	536049 T	09-03-1998
		EP	0768284 A	16-04-1997
		ES	2107515 T	01-12-1997
		WO	9307095 A	15-04-1993
		JP	6503300 T	14-04-1994
		PL	299429 A	21-03-1994
		PL	170583 B	31-01-1997
		SK	70593 A	06-10-1993
		US	5545596 A	13-08-1996
		US	5582455 A	10-12-1996
WO 9600194 A	04-01-1996	FR	2721599 A	29-12-1995
		BR	9506042 A	05-08-1997
		CA	2169936 A	04-01-1996
		CN	1137262 A	04-12-1996
		CZ	9600562 A	14-08-1996
		EP	0722427 A	24-07-1996
		HU	75982 A	28-05-1997
		JP	9502420 T	11-03-1997
		· PL	313115 A	10-06-1996
		US	5837629 A	17-11-1998
US 5393593 A	28-02-1995	CA		26-04-1992
		DE	69111558 D	31-08-1995
		DE		21-03-1996
		EP	- 0482535 A	29-04-1992
		ES	2077763 T	01-12-1995
		JP	1996987 C	08-12-1995
		JP	4275943 A	01-10-1992
	, in the industri	JP		05-04-1995
		KR		14-03-1994
EP 0705800 A	10-04-1996	DE		09-07-1998
		DE	69502790 T	04-02-1999
		JP US		18-06-1996 10-03-1998

Form PCT/ISA/210 (patent family annex) (July 1992)

그는 그 이 아이는 사람이 하는 사람이 되는 것이다.	[1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1] - [1
	일 보다. 그리 전하다 남자, 사용하루 하다 그는 그 그 그 그는 그는 그 그 없다.
- 경우하다 - 이번 사람이 없는 것 같아 보이고 있다. 그는 것이 말씀하는	그렇게 하시아 사람들이 한 사람이 들어 보는 사람이 되는 사람이 되는 사람이 없다.
	되다. 그림의 하하는 경우를 받았습니다. 그리는 그리는 그리는 사람들이 되었
그는 가는 호급한 환경인 교육자 등 시간 이 본지가 회문화	리스 (Paris) - Paris (Barata) - 12 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1
그렇고의 사람들은 바람이들이 받는데 나가는 그 아니는 것이다.	등 리리는 작가 가게 살아가 있다는 것이 없는 것이 없는 것이 없다.
그림에 하는 소리를 들는 경에 되면 보는 것이 되어 하고 있었다.	: 요리하다 사기 전략상품없이 되었다는 상 그 이 그는 경기 점이 되었다.
그렇는 이 안 하시아 사람들이 얼마나 있는데 아이들이 되니까 않아야 했다.	
	교회 이 그 때문, 생각을 처음하실일이 모습니다고 하는데 말하는데 다
이름화에서는 전환 가능하다면서 하는 사람이 이번 생각하고 있다.	면하다 하는 아이를 하고 하다면 하는 사람들이 없다는 것이다. 그렇게 되었다는 것이다.
그릇 그림에 대학생님들이 가지를 만입하다. 그림은 생생들이	트리트 이번 이번 때문화학을 모습하는 경험이 이 보호들은 부리는 것이다.
말함하는 말하고 말을 들어 있는데 하는 생님이 모모를 통해야	
	(1) 전 10 전
	화가 되면 사람이 되는 사람이 가셨다면 가셨다는 그들은 사람들이 되었다.
그리스 그 이 이 경험으로 하는 물론이 유지 않는 사람들이 모르다.	회사의 시민들은 사람들이 가입니다. 그는 이 사람들이 나가 하는 사람들이 가입니다.
	즐거리가 시민은 있는 비용을 하면서 이 중인 중 인터스에도 영급한 그림은 그 그는
그는 사람들은 사람들이 아름답지 모을이 많을 것입니다.	막이면 네트를 살아가 살아야 하면 하는 사람들이 가득하는 것이다.
그들도 제 발생으로 됐다. 그 작은 사람들은 바다는 어디로 토토했다.	를 보고 있는데 있는데 그 사람들은 그를 보고 있다. 그런 그런 그를 보고 있는데 그를 보고 있는데 그를 보고 있다. 물로 보고 있는데 그를 보고 있는데 그를 보고 있는데 그를 보고 있는데 그를 보고 있다.
그들이 그 되었다는 하실시다. 한 일상되면 그리다 그 없었다면 보였다.	
	하다는 사람이 사람들은 사람들이 되는 것은 사람들은 사람들은 사람이 되었다.
그 가게 되었다는 바람들이 얼마를 살아가는 다음을 살아갔다.	성용하다는 소문에 한국으로 논리를 가면하고 만족 그녀를 보다고 하다.
	실고하는 이번 역사하고 주를 하면하다. 그리라를 보고 있다고 하다 이번
그렇게 맛있다면 맛있다면 하다면 하는 것이 하는 것이 하는데 하는데 없었다.	불교 하는 살 하면 불어진 그래에는 이상이 사람들이 살아 들어 들었다.
	하는 생성의 회사 발표를 가장 하는 경우 하다 있습니 환경을 갖고했다. 그 그
	그들은 사람들은 아이들은 사람들이 하는 그들은 그릇이 살아왔다면 그 사람들이 모르는
	[연구] [10] [10] [10] [10] [10] [10] [10] [10
그러는 항상 사는 사람들은 한 경찰 나는 이 기가를 받았다.	(하는 기업은 그 경기에서 되었다. 그 얼마나는 아니라 사람이 되었다.
그는 이번 나를 살아왔었다. 하다 네 하고 하다 보았다면 얼마?	보다하게 본론 이름이었다면 하는 그리는 그렇게 하다니까 하다면 하는데 하는데
	() (18 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 19 1 - 1
마음을 하면 한다. 그래한 소설 그들은 살이 가는 장면을 함께 다른	20. 회의 이 집 함께 이용화화 전 보고 있을 하셨습니다. 요즘이 이름이
[제집] [18]	
강에 가는 일일 전혀, 몇몇분이 돼 것 같니까? 얼룩했다.	
그 문학 그렇게 살아왔다면 맛없게 살아왔다. 사이로 불쾌 없었다.	
	임근 () 그들은 그래 이렇지는 돌아왔습니다. 그리고 있는 이 그리는 그는
그가 하는 사람들이 가까지 하는 생각들은 가는 가는 사람들이 되었다. 회	회사 (문항의 최고 회문을 통한 등이 남은 사용하는 유명을 받는 사용이다.
그리 본 사용 바다 하셨다. 그는 살이 가지 않는데 하다.	
마시아 아버리를 잃었습니다는 그를 가능하는 어떻게 하다.	
그렇게 얼마속한 사람들 악병 등 나는 것이 하는 경험을 받았다.	
그리고 안전 전 아이스로 맞이 아이스를 잃었다. 그리고 아니라 작은	
그리에 그는 소리를 즐겁지다고 하고 있는 물건 속 모르는 아름다면 모르는	취임 일 하는 해도 회사들은 그가 그는 전기를 다음하는 것이라고 그는 스
그램 시회의 등에 없어요. 하는 하나면 모르는 그릇 말았다.	H : 사람들은 사람들은 사람들은 사람들은 사람들은 사람들은 사람들은 사람들은
이 그는 살이 되었는데 모든 보고 하는 것이 없었다. 모든	2011년 1월 18일 2012년 4일 기타를 다듬다면 보다 보다 다른다.
	공연, 이 아니면서, 발생하는 사용이, 고마니는 아니라 생생들이 된다. (B.C.) 모든
	발생 시민과의 바로 살림이 얼마나 아니라 이 보다는 사람이 되었다.
	可能是一点性能致,他们也是一点的原则是这样的。